

AD-A045 725

UTAH UNIV SALT LAKE CITY
NEGATIVE MOLECULAR IONS.(U)
AUG 77 J P SIMONS

F/G 7/4

UNCLASSIFIED

1 OF 1
ADA
045725

ARO-12031.10-C

DAAG-29-74-G-0221
NL



END
DATE
FILMED

11-77

DDC

ARC-V2031.10-C

12

J

AD A 045725

NEGATIVE MOLECULAR IONS

Final Report

Dr. John P. Simons

August 17, 1977



U. S. ARMY RESEARCH OFFICE

DAAG-29-74-G-0221

University of Utah
Salt Lake City, Utah

AD No. _____
DDC FILE COPY

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

⑨ Final rept 15 Jun 74 - 14 Jun 77

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER P-12031-G ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) NEGATIVE MOLECULAR IONS. ✓	5. TYPE OF REPORT & PERIOD COVERED Final 6/15/74 - 6/14/77	
7. AUTHOR(s) ⑩ DE. John P./Simons	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Utah Salt Lake City, Utah 84112 ✓	8. CONTRACT OR GRANT NUMBER(s) ⑮ DAAG-29-74-G-0221/rln	
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) ⑮ ARO ⑰ 12031.10-C	12. REPORT DATE 8/16/77 ✓	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. ⑫ 32 p.	13. NUMBER OF PAGES	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA	15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
18. SUPPLEMENTARY NOTES The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Negative Ions, Atmospheric Ions, Electrons		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See Following Page		

⑰ 17 Aug 77
D D C
OCT 26 1977
RESOLVED
C

362 900 ⑧

Table of Contents

I. Historical Perspective	3
II. Review of the Theoretical Methods Employed	7
III. Brief Survey of Some Results	17
A. OH^- : Our First Comparison with Experiment	
B. BeH^- : An Experimentally Understudied Anion	
C. CN^- and BO^- : A Well-Known Ligand and its Isoelectronic Partner	
D. Li_2^- : The Building Block of Small Metal Cluster Anions	
E. LiF^- , LiC^- , LiH^- , NaH^- , BeO^- : Binding of Electrons to Dipoles	
F. Other Results: Checks with Experiments and Prediction of New Molecules	
G. Tabular Overview of Results Obtained to Date	

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
J S	
BY	
DISTRIBUTION/AVAILABILITY CODES	
SPECIAL	
A	

Abstract

Having been successful in our studies of isolated (gas-phase) OH^- , NH_2^- , BeH^- , CN^- , BO^- , Li_2^- , and NO_2^- , we are now in a good position to further develop this area by 1) extending our calculations to chemically related molecules, e.g., SH^- , PH_2^- , MgH^- , etc., and 2) beginning to look into the hydration (or other solvation) of the species whose gas-phase properties we already know. Both of these avenues of research are feasible. We now have more powerful computer programs (MOLECULE) which should permit us to study the heavier analogs mentioned above. Moreover, we have also recently gained the experience needed to include solvation effects in our studies of those anions which we earlier studied as isolated systems. The hydration may be described either in terms of "model" H_2O molecules which are simply point charges distributed to represent the dipole moments of the surrounding solvents, or in terms of real ab initio H_2O molecules. The ab initio solvent studies will probably be restricted (by cost) to cases in which only one, two, or three solvent molecules surround the anion. The "model" solvent calculations might not be sufficient; we can only answer these questions by trying the computation, although some existing work on hydration by Morokuma and by ourselves has been encouraging.

Because we have successfully carried out many calculations on anions using the method described here in, a critical evaluation of the theory is available, and therefore, calculations on many other chemically important species can now be undertaken with some confidence. In addition to the above two extensions of our work, we are specifically interested in pushing on toward obtaining accurate electron detachment energies, geometries, and charge densities for the following interesting ions: O_4^- , CO_3^- , NO_3^- and other anions which play important roles in atmospheric chemistry. (O_3^- and NO_2^- have already been characterized). Now that we have more powerful computer programs available,

such studies are within our range (with the MOLECULE program a calculation on NO_2^- with 30 contracted Gaussian orbitals costs less than \$50). Of course, the time and computer costs needed to perform a complete investigation of all the species listed above may well exceed the time interval of this proposal and the funds presently available to us. However, the mere fact that the geometry and stability of O_4^- remain as unsettled problems is sufficient to justify a concentration of work on this problem.

We also plan to expand our research into novel new anions whose properties have not been determined experimentally. Our work on the binding of electrons to (closed-shell) highly polar molecules (LiH , LiF , BeO , LiCl , NaH , etc.) will be extended to include model studies in which the potential energy field of the polar molecule is replaced (e.g. for a diatomic) by that of two point charges ($\pm q$) separated by the experimental bond length (with $Rq = \mu_{\text{exptl}}$) plus a "core" (e.g., $1s^2$ for Li , $1s^2 2s^2 2p^6$ for Na) on the electropositive atom. In this manner we hope to extend our investigation to systems containing several (a cluster) such polar molecules. Our initial results from this kind of a model calculation are very encouraging.

I. Historical Perspective

In 1968 Berry¹ reviewed the experimental and theoretical progress which had been made toward understanding the stabilities and bonding characteristics of small isolated (gas-phase) negative ions. In this review Berry commented as follows:

"For the theorist, electron affinities and other properties of negative ions pose greater difficulties than do properties of neutrals or positives, insofar as electron correlation plays a relatively larger part in determining the properties of a negative ion than it does in other species. In fact, electron affinities are frequently about the same size as the differences between correlation energies in atoms and in the corresponding negative ions."

As an example of the magnitudes of electron correlation effects, one need only consider the results of our calculations on the vertical ($R = 1.718$ au) electron detachment energy ($X^1\Sigma^+ OH^- \rightarrow X^2 \pi_i OH$) of OH^- . Using an atomic orbital basis consisting of twenty Slater-type orbitals (STO's), we obtained a Koopmans' theorem approximation to the detachment energy equal to 3.06 eV. The energy difference between two separate SCF calculations (ΔSCF), one on OH^- and one on OH , carried out within the same basis was equal to - 0.20 eV; the difference between Koopmans' theorem and ΔSCF represents the effects of allowing the orbitals to relax upon removal of the π electron. Finally, our best computed energy difference², which contains effects of electron correlation through third order, was 1.76 eV which is in good agreement with both Branscomb's early experiments³ and Lineberger's more recent laser detachment results.⁴ The difference between 1.76 eV and the ΔSCF value of -0.2 eV represents the effects of electron correlation. These effects are indeed as large as the entire electron affinity of OH ; moreover, this result is not atypical.

Because the treatment of both orbital relaxation and electron correlation effects in a sufficiently rigorous manner is an absolute necessity in any reliable scheme for computing properties of anions, theoretical progress toward understanding negative ions has been made rather slowly. Quite simply put,

it is difficult to include correlation effects to a high enough order to guarantee precision ± 0.2 eV in computed ion-neutral energy differences. In Berry's review article, his assessment of the state of quantum chemical research on anions involved briefly mentioning the works of Pekeris⁵ on H^- , Weiss⁶ on Li^- , Na^- , and K^- , Clementi and co-workers⁷ on several atomic ions, Sinanoglu⁸ on C^- , O^- , and F^- , Taylor and Harris⁹ on H_2^- , Wahl and Gilbert¹⁰ on halogen diatomics, and Cade¹¹ on OH^- , CH^- , SiH^- , SH^- , and PH^- . Therefore, in 1968 it would have been fair to say that negative molecular ions were not yet within the class of species which could be conveniently studied by existing quantum chemical methods. On the other hand, the development of modern laser technology was making available to the experimentalist new tools to use in carrying out high precision photodetachment and photoelectron spectroscopy studies of gas-phase anions. Thus, even in 1968 a great deal of experimental progress was beginning to be made. These experimental developments made a parallel development of theoretical methods and models aimed at better understanding negative ions a necessary and quite natural step in the scientific progress in this area.

In 1973 Simons and Smith¹² published an article in which they attempted to use equations of motion (EOM) techniques¹³ to express the vertical electron affinity (EA) or detachment energy (DE) of a closed-shell species in a manner which treated orbital relaxation and electron correlation through third order in perturbation theory (the difference between the coulombic interaction and the Hartree-Fock interaction being the perturbation). This developmental paper was followed by other formal papers by Simons, Jørgensen, Jordan, and Chen¹⁴⁻¹⁵ in which small deficiencies in the original theory were corrected and connection made with the recent Green's function developments of Cederbaum¹⁶, Pickup and Goscinski¹⁷, Purvis and Öhrn¹⁸, and Freed¹⁹. The result of these papers was a method which permits the direct calculations of EA's and DE's, of closed-shell

species, which are accurate through third order.

In succeeding publications^{2,20-26} the third order EOM theory was applied to studies of the stability and bonding characteristics of several molecular anions (and cations). Calculations of the electron affinities of OH, BeH, NH₂, CN, and BH provided theoretical support (to within ± 0.2 eV) for existing experimental measurements. Studies of the EA's of BO and Li₂ resulted in theoretical predictions for species where good experimental data is not available. Calculations of the EA's of LiF, LiCl, LiH, NaH, and BeO have led to predictions to both the existence and the stabilities (with respect to electron loss) of the anions of these species. Jordan⁹² has also examined the dimer anion (LiH)₂⁻; Simons and Jordan⁹³ have recently found Be₂⁻ to be stable even though Be₂ is unbound. Very recently, the ion LiCl⁻ was observed by Lineberger²⁷ thereby verifying the theoretical prediction of Jordan *et al*⁷⁷. The precise nature of some of the above calculations together with the principal conclusions of these works are treated later in this proposal.

In the time since Berry's 1968 review article was completed and for a few years prior to that date, several ab initio calculations, in addition to those mentioned above, were performed on molecular anions which are of chemical interest. These studies include the following works: Clementi²⁸ (N₃⁻), Lipscomb²⁹ (PO⁻), Krauss³⁰ (BH₄⁻, O₂⁻) Kaufman³¹ (O₃⁻), Csmizmadia³² (CH₃⁻, NH₂⁻), Pfeiffer³³ (NO_s⁻), Popkie³⁴ (C₂⁻), McLean³⁵ (OCN⁻, SCN⁻), Wahl³⁶ (Cl₂⁻, F₂⁻), Fink³⁷ (OH⁻, NH₂⁻, CH₃⁻, BH₄⁻), Geller³⁸ (BH₂⁻), Thulstrup³⁹ (NO⁻), Peyerimhoff⁴⁰ (BeH₃⁻), Heaton⁴¹ (NH₂⁻), Schaefer⁴² (NO₂⁻), Thulstrup⁸⁴ (C₂⁻), O'Hare⁸⁵ (NF⁻, NS⁻, PF⁻, SF⁻). This list is by no means a complete tabulation of all work done on negative molecular ions; it is simply meant to indicate the kinds of systems which have been studied as well as approximately the number of calculations which have been performed to date. Although it is true that a reasonably large number of ab initio calculations have been carried out

for diatomic and small polyatomic species, very few of the studies referenced above include any electron correlation effects. Most of these calculations have been done at the SCF-level within small-to-moderate size bases. Therefore, the EA's which have been obtained in this manner are probably not reliable. On the other hand the equilibrium geometries and charge densities obtained in the above SCF-level works may not be any less accurate than the results of analogous calculations on neutral species; electron correlation effects are not as dominant as in determining EA's. Nevertheless, it is our feeling that most of the reliable work on negative ions has been, and will continue to be, characterized by a careful treatment of electron correlation and charge relaxation. For this reason, the remainder of this proposal will be restricted to discussion of results and proposals for studies which treat correlation in an ab initio manner, except in those cases where simple chemical models are introduced to permit a qualitative understanding of more complex systems.

With this brief survey of the developments made since 1968 as a background, let us now turn to a more detailed discussion both of the most recently utilized methods and the results which have been obtained with these methods. In Sec. II we review the foundation of the direct-calculation approach of refs. 12-19. Sec. III contains a survey of results on OH^- , NH_2^- , BeH^- , CN^- , BO^- , LiF^- , LiCl^- , LiH^- , NaH^- , BeO^- , NO_2^- in which the effects of orbital relaxation and correlation have been included. Specific attention is paid to stabilities (EA or DE), geometries (R_e , θ_e), vibrational frequencies, dissociation energies, and charge densities of these anions. In Sec. IV we review the conclusions which have been reached thus far and we make concrete proposals for research in areas which seem to show special promise for future development.

II. Review of the Theoretical Methods¹⁵ Employed

The electron propagator or the one-electron Green's function has been used for some time^{16,18,20-26,43-46} in the study of electron spectroscopy. The advantages of using the electron propagator arise because the transition energies and the transition strengths are obtained directly as poles and residues of the propagator, respectively. Several alternative procedures for decoupling the Equation-of-Motion for the electron propagator have been developed. In this analysis we use the superoperator formalism of Goscinski and Lukman⁴⁷ as the framework for our development of an electron propagator which is consistent through third order. In an alternative derivation using the Equation-of-Motion formalism of Rowe⁴⁸, Simons and Smith¹² attempted to obtain an Equation-of-Motion which was consistent through third order. Purvis and Öhrn⁴⁹ pointed out some deficiencies in the theory of Simons and Smith; these deficiencies are mentioned again in this section. We show further how the electron propagator can be obtained consistent through third order. The consistency is made more transparent by demonstrating that all second and third order self energy diagrams of Cederbaum¹⁶ are included in our formalism.

The definition of the spectral electron propagator⁴⁴ can be written within the superoperator formalism as

$$\underline{G}(E) = (\underline{a} | (E\hat{I} - \hat{H})^{-1} | \underline{a}) \quad (1)$$

where \hat{I} and \hat{H} are the superoperator identity and hamiltonian respectively and the \underline{a} are a set of annihilation operators $\underline{a} = \{a_i\}$, which are arranged in a super row vector. The superoperator scalar product is defined in the conventional fashion⁴⁷. The superoperator resolvent $(E\hat{I} - \hat{H})^{-1}$ can be approximated via the inner projection technique and the propagator then takes the form

$$\underline{G}(E) = (\underline{a} | \underline{h}) (\underline{h} | E\hat{I} - \hat{H} | \underline{h})^{-1} (\underline{h} | \underline{a}) \quad (2)$$

where \underline{h} is a projection manifold which, if chosen to be complete and orthonormal, makes Eqs. (1) and (2) identical. The operator space

$$\{h_1, h_3, h_5, \dots\} = \{a_i, a_i^\dagger a_k a_l, a_i^\dagger a_j^\dagger a_k a_l a_r, \dots\}, k>l, i>j, k>l>r \dots \quad (3)$$

spans the manifold \underline{h} . We now discuss appropriate selections of \underline{h} which, in conjunction with our choice of the reference state, ensure that the electron propagator is calculated correctly through third order in the electronic interaction.

It is well known^{17,45} that the projection manifold $\underline{h}_1, \underline{h}_3$ in connection with the Hartree-Fock (HF) ground state is able to give the electron propagator correct through second order in the electronic interaction. Our experience^{2,20,26} tells us that second order calculation of EA's are not sufficiently precise to be useful. (except in well-understood special cases which are discussed

below). We demonstrate how, using a correlated ground state and the same projection manifold, we are able to get the electron propagator correct through third order in the electron interaction.

The effect of including \underline{h}_5 in the projection manifold, where the HF ground state is used as reference state, has been discussed by Tyner *et al*⁵⁰, and from their analysis it is clear that \underline{h}_5 introduces terms which are at least fourth order in the electronic interaction, independent of the choice of reference state. We therefore concentrate on using $\underline{h}_1, \underline{h}_3$ as our projection manifold in our search for a theory which is consistent through third order.

As the reference state in our analysis we use a correlated wavefunction given by

$$\begin{aligned}
 |0\rangle = N^{-1/2} \{ & 1 + \sum_{p\delta} (K_{\delta}^p a_p^+ a_{\delta}) + \sum_{\substack{m>n \\ \alpha>\beta}} (K_{\alpha\beta}^{mn} a_m^+ a_n^+ a_{\beta} a_{\alpha}) \\
 & + \sum_{\substack{m>n>p \\ \alpha>\beta>\delta}} (K_{\alpha\beta\delta}^{mnp} a_m^+ a_n^+ a_p^+ a_{\alpha} a_{\beta} a_{\delta}) + \dots \} |HF\rangle
 \end{aligned} \quad (4)$$

where the \underline{a}^+ are a set of HF creation operators and where indices m, n, p, q ($\alpha, \beta, \delta, \gamma$) refer to unoccupied (occupied) spin orbitals in the HF ground state and i, j, k, l, r are unspecified spin orbitals. We take the correlation coefficients from Rayleigh-Schrödinger perturbation theory

$$\begin{aligned}
 K_{\delta}^p = \sum_{\substack{m>n \\ \alpha>\beta}} \{ & \langle p\alpha || mn \rangle \delta_{\delta\beta} - \langle p\beta || mn \rangle \delta_{\alpha\delta} + \langle \beta\alpha || \delta m \rangle \delta_{np} - \langle \beta\alpha || \delta n \rangle \delta_{pm} \} \\
 & \times \frac{\langle mn || \alpha\beta \rangle}{(\epsilon_{\delta} - \epsilon_p)(\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_n - \epsilon_m)} + \text{higher order terms} = K_{\delta}^p(2, 3, \dots) \\
 & \text{in the electronic interaction}
 \end{aligned} \quad (5)$$

$$K_{\alpha\beta}^{mn} = \frac{\langle mn || \alpha\beta \rangle}{\epsilon_{\alpha} + \epsilon_{\beta} - \epsilon_m - \epsilon_n} + \text{higher order terms in the electronic interaction} = K_{\alpha\beta}^{mn} (1,2,\dots) \quad (6)$$

$$K_{\alpha\beta\delta}^{mnp} = K_{\alpha\beta\delta}^{mnp} (2,3,\dots) \quad (7)$$

where the first number in the bracket indicates the lowest order in the electronic interaction. The ϵ_i indicate HF orbital energies and the two electron integral $\langle mn || \alpha\beta \rangle$ refers to the charge densities $m\alpha$ and $n\beta$ and

$$\langle mn || \alpha\beta \rangle = \langle mn | \alpha\beta \rangle - \langle mn | \beta\alpha \rangle \quad (8)$$

in our analysis we consider the projection manifold $\{\underline{h}_1, \underline{h}_3\}$ where the \underline{h}_3 space for convenience has been redefined as

$$\underline{h}_3 = \{a_{ik}^\dagger a_{i1} + \langle a_{i1}^\dagger a_k \rangle a_k - \langle a_{i1}^\dagger a_k \rangle a_{i1}\} \quad (9)$$

The choice of the subspace \underline{h}_3 ensures that this space is orthogonal to \underline{h}_1

$$(\underline{h}_1 | \underline{h}_3) = 0 \quad (10)$$

even for a correlated reference state. We also have the following orthogonality relations

$$(\underline{h}_1 | \underline{h}_1) = \underline{1}, (\underline{h}_3 | \underline{h}_3) = \underline{S} (0,2,3,\dots) \quad (11)$$

Using Eqs. (10) and (11), Eq. (2) can be partitioned into the form

$$\begin{aligned} \underline{G}^{-1}(E) &= (\underline{h}_1 | \hat{E}\hat{I} - \hat{H} | \underline{h}_1) - (\underline{h}_1 | \hat{H} | \underline{h}_3) (\underline{h}_3 | \hat{E}\hat{I} - \hat{H} | \underline{h}_3)^{-1} (\underline{h}_3 | \hat{H} | \underline{h}_1) \\ &= \underline{E}\underline{1} - \underline{A} - \underline{B} \underline{D}^{-1} \underline{C} \end{aligned} \quad (12)$$

where the matrices \underline{A} , \underline{B} , \underline{C} and \underline{D} are defined as

$$\begin{aligned}\underline{A} &= (\underline{h}_1 | \hat{H} | \underline{h}_1) \\ \underline{B} &= (\underline{h}_1 | \hat{H} | \underline{h}_3) \\ \underline{D} &= (\underline{h}_3 | E\hat{I} - \hat{H} | \underline{h}_3) \\ \underline{C} &= (\underline{h}_3 | \hat{H} | \underline{h}_1)\end{aligned}\tag{13}$$

We will now make an order by order analysis of Eq. (12) in which we retain only those terms which are zeroth, first, second, or third order in the electronic interaction. Since the \underline{B} and \underline{C} matrices are at least of first order¹², we need to consider only that part of the \underline{D} matrix which is zeroth and first order. This constrains the indices in the projection manifold \underline{h}_3 to be of the form $a_m^\dagger a_\alpha a_\beta$ $\alpha > \beta$ or $a_\alpha^\dagger a_m a_n$ $m > n$ since operators such as $a_m^\dagger a_n a_\alpha$ lead to matrix elements in the \underline{D} matrix which are at least of second order. The resulting subspace \underline{h}_3 is thus identical to that used in calculating the electron propagator correct through second order. To calculate the electron propagator through third order in the electron repulsions, we thus need to obtain the \underline{B} and \underline{C} matrices through second order, the \underline{D} matrix through first order, and the \underline{A} matrix through third order.

Previous attempts¹² to obtain the electron propagator correct through third order have used as reference state

$$0 = N_0^{-1/2} \left(1 + \sum_{\substack{m>n \\ \alpha>\beta}} K_{\alpha\beta}^{mn} a_m^\dagger a_n^\dagger a_\alpha a_\beta \right) |HF\rangle\tag{14}$$

theory. In calculating the \underline{B} (\underline{C}) and \underline{D} matrix elements correct through second and first order, respectively, no changes are obtained from considering the higher correlated ground state in Eq. (4). The matrix elements of \underline{B} , \underline{C} , and \underline{D} are given by

$$B_{i,\alpha\beta} = -\langle im|\alpha\beta\rangle - \frac{1}{2} \sum_{p,q} \langle im|pq\rangle K_{\alpha\beta}^{pq} + \sum_{\gamma,p} \left[\langle i\gamma|p\alpha\rangle K_{\beta\gamma}^{mp} - \langle i\gamma|p\beta\rangle K_{\alpha\gamma}^{mp} \right] \quad (15)$$

$$B_{i,n\alpha m} = \langle i\alpha|mn\rangle + \frac{1}{2} \sum_{\gamma\delta} \langle i\alpha|\delta\gamma\rangle K_{\delta\gamma}^{mn} + \sum_{\gamma p} \left[\langle ip|\gamma n\rangle K_{\alpha\gamma}^{mp} - \langle ip|\gamma m\rangle K_{\alpha\gamma}^{np} \right] \quad (16)$$

$$\underline{C}^+ = \underline{B} \text{ (through second order)} \quad (17)$$

$$D_{nam,\delta p\gamma} = 0, \quad (18)$$

$$\begin{aligned} D_{nam,q\beta p} = & \delta_{nq} \delta_{\alpha\beta} \delta_{mp} (\epsilon_m + \epsilon_n - \epsilon_\alpha) - \delta_{qn} \langle m\beta||p\alpha\rangle - \delta_{pm} \langle n\beta||q\alpha\rangle \\ & + \delta_{qm} \langle n\beta||p\alpha\rangle + \delta_{\alpha\beta} \langle mn||pq\rangle + \delta_{pn} \langle m\beta||q\alpha\rangle, \end{aligned} \quad (19)$$

$$\begin{aligned} D_{\delta p\gamma,\alpha q\beta} = & -\{\delta_{\delta\alpha} \delta_{pq} \delta_{\gamma\beta} (\epsilon_p - \epsilon_\delta - \epsilon_\gamma) - \delta_{\gamma\beta} \langle \delta q||\alpha p\rangle - \delta_{\delta\alpha} \langle \gamma q||\beta p\rangle \\ & + \delta_{\gamma\alpha} \langle \delta q||\beta p\rangle - \delta_{pq} \langle \delta \gamma||\beta \alpha\rangle + \delta_{\delta\beta} \langle \gamma q||\alpha p\rangle \end{aligned} \quad (20)$$

In the \underline{A} matrix we need to include all terms up to third order. The \underline{A} matrix elements obtained by using Eq. (14) as a reference state need to be modified by third order terms which result from interaction between the singly excited states and the HF ground state. The triply excited states which also result from a second order Rayleigh-Schrödinger perturbation calculation do not introduce third order terms. We thus have to add to the \underline{A} matrix elements given in ref. [12] the terms δA_{ij}

$$\delta A_{ij} = \sum_{\delta\beta} \frac{\langle j p | | i \delta \rangle \langle \delta \beta | | m n \rangle \langle m n | | p \beta \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\delta + \epsilon_\beta - \epsilon_m - \epsilon_n)} \quad (A3)$$

$$+ \sum_{\delta\beta} \frac{\langle j \delta | | i p \rangle \langle p \beta | | m n \rangle \langle m n | | \delta \beta \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\delta + \epsilon_\beta - \epsilon_m - \epsilon_n)} \quad (A4)$$

$$+ \sum_{\delta\alpha\beta} \frac{\langle j p | | i \delta \rangle \langle \delta n | | \beta \alpha \rangle \langle \alpha \beta | | p n \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_n)} \quad (A5)$$

$$+ \sum_{\delta\alpha\beta} \frac{\langle j \delta | | i p \rangle \langle \beta \alpha | | \delta n \rangle \langle p n | | \alpha \beta \rangle}{(\epsilon_\delta - \epsilon_p)(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_n)} \quad (A6)$$

The A matrix of ref. [12] is

$$A_{ij} = \delta_{ij} \epsilon_i + \sum_{k,l} \langle i k | j l \rangle F_{kl} \quad (21)$$

$$F_{kl} = \sum_{\alpha > \beta, p} K_{\alpha\beta}^{pk} K_{\alpha\beta}^{pl} - \sum_{p < q, \alpha} K_{\alpha l}^{pq} K_{\alpha k}^{pq} \quad (22)$$

We thereby have calculated the electron propagator consistently through third order.

A comparison with a diagrammatic perturbation expansion of the self-energy⁸⁶ makes it further transparent that we have really included all terms through third order in our analysis of the electron propagator. In Fig. 1 we have displayed the terms A3 - A6 as diagrams using the rules of Brandow⁵¹ which combine the Goldstone diagrams with the antisymmetrized vertices of Hugenholtz. The diagrams labelled A3 - A6 are identical to the third order diagrams given by Cederbaum¹⁶, in which dots refer to antisymmetrized vertices. The diagrams A3 - A6 were shown by Purvis and Öhrn⁴⁹ to be the only missing third order

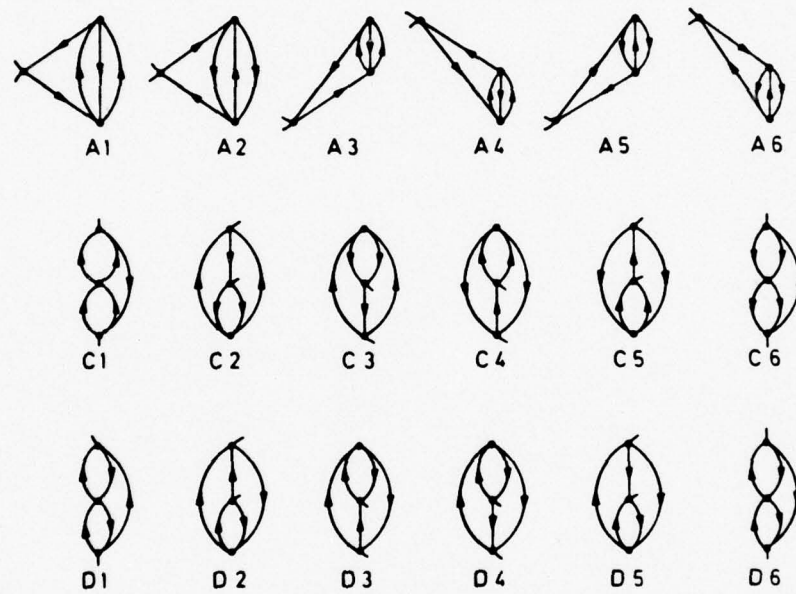


Fig. 1

diagrams which evolve from a theory where the reference state is given by Eq. (14). The analysis of Purvis and Öhrn considered $(\underline{h}_3|E\hat{I} - \hat{H}|\underline{h}_3)$ as two matrices; \underline{u} which contains E and orbital energies (zeroth order terms) and \underline{M} which contains the two electron integrals (first order terms). Making use of the identity $(\underline{u} + \underline{M})^{-1} = \underline{u}^{-1} - \underline{u}^{-1} \underline{M}(\underline{u} + \underline{M})^{-1}$ to expand the inverse, Purvis and Öhrn identified the diagrams C1 - C6 and D1 - D6 of Cederbaum¹⁶ to originate from the $\underline{B}\underline{D}^{-1}\underline{C}$ term while the diagrams A1 - A2 were found to arise from the \underline{A} matrix previously given in ref. [12]. We thus have accounted for all third order diagrams which arise from an expansion of the self energy. The electron propagator calculation thus needs to use the second-order correlated ground state given in Eq. (4) as a reference state and the subspace $\{\underline{h}_1, \underline{h}_3\}$ given by Eq. (3) as the projection manifold to be correct through third order.

We have shown how the electron propagator can be obtained correctly through third order. Our development stresses the fact that a complete treatment of the inverse of the \underline{D} matrix is needed to guarantee that all desired terms are included. Computational applications have so far only been carried out using a diagonal approximation to the D matrix. This situation is unsatisfactory and should be improved. A unitary transformation which brings the \underline{D} matrix closer to diagonal form is related to the theory of linear response as discussed by Jørgensen and Purvis⁵². Using this kind of procedure we would expect to get an approximation to the propagator which would be nearly complete through third order. The energy shifted denominators which result from evaluating the \underline{D} matrix, correspond to the result of summing certain classes of diagrams to infinite order, which implies that the electron propagator treatment has the computational advantage of expressing these summations in closed form. In a diagrammatic summation of self-energy diagrams one has to explicitly account for each energy shifted denominator through each order. We finally note that the side shifted diagrams given in Fig. 1 do not appear in the original third

order theory of Simons and Smith¹² for calculating ionization potentials and electron affinities. These diagrams result from using a more highly correlated wavefunction than the one considered by Simons and Smith as the reference state.

With this derivation of the needed third order equation accomplished, let us now turn to a more detailed description of selected results which have been obtained by making use of the propagator approach. Recall that we are limiting the discussion to studies which have treated electron correlation effects in an ab initio manner. The anions which we have chosen to discuss in some detail can be divided into several classes. NH_2^- , OH^- , BeH^- , are hydrides whose parents have a half-filled orbital to which the "extra" electron is added. CN^- , BO^- , and NO_2^- are ions whose parents also have half-filled orbitals. All of the above ions are closed-shell species. Li_2^- and Be_2^- are open-shell ions which are formed by adding an electron either to an antibonding (Li_2^-) or bonding (Be_2^-) molecular orbital of the closed-shell parent. LiF^- , LiCl^- , LiH^- , NaH^- , and BeO^- are each formed by adding an electron to an essentially nonbonding orbital of the very polar neutral parent; in these ions correlation and relaxation are not very important because the "extra" electron resides in an orbital which is localized on the "back" end of the electropositive atom where it encounters little dynamic interaction with the other electrons. It is clear that our studies of anions have covered a wide range of chemically quite different species in which the factor (or factors) governing the binding of the electron to the parent include dipole forces, valence attraction of a half-filled orbital, polarization of charge, and formation of new bonding orbitals (Be_2^-).

III. Brief Survey of Some Results

A. OH⁻: Our First Comparison With Experiment

In carrying out the calculations on OH⁻ described here², we employed an atomic orbital basis consisting of Slater-type functions whose orbital exponents were taken from the bases of Cade⁵³ for HO⁻, and of Cade and Huo⁵⁴ for ·OH. Information describing our basis and the essential results of the SCF calculation on the parent X¹Σ⁺OH⁻ for this basis are given in table A1. Note that the basis used in this work is not very large.

As shown in table A2, the vertical detachment energies computed using the basis of table A1 are within 0.10 eV of the experimental result quoted by Lineberger et al⁴. An important observation which should be made here is that the basis given in table A1 is capable of yielding a very accurate detachment energy. Our results show that the theory of molecular electron affinities and ionization potentials in ref. (12) is capable of yielding the vertical electron detachment energy of X¹Σ⁺OH⁻ to within 0.1 eV. It has also been demonstrated that a highly accurate description of the core orbital of OH⁻ is not essential to an accurate calculation of the ²Π_i valence electron detachment energy. Finally, an investigation of the roles of orbital relaxation and correlation energy change in determining the ion-molecule energy difference has led to the conclusion² that both of these effects must be treated properly in any study of negative molecular ions unless one knows that the "extra" electron is essentially uncorrelated (perhaps by spatial localization) with the other electrons. As discussed in part E of this section, such is the case for the family of anions formed by adding an electron to a highly polar closed-shell molecule.

Table A1

20-Function Hartree-Fock Wavefunction for OH⁻. R = 1.781 au, E = -75.3801 au,

$$\epsilon_1 = -20.22091, \epsilon_2 = -.94178, \epsilon_3 = -.27867, \epsilon_1 = -.12616$$

σ atomic orbitals	1σ	2σ	3σ	π atomic orbitals	1π
01s (7.0168)	.9721	-.1645	.1213	02p (2.0624)	.5857
02s (2.8646)	.1268	.8711	-.0336	02p' (3.7529)	.1949
02p (2.1172)	-.0349	.0490	.3761	02p'' (0.7128)	.3246
01s' (12.3850)	.0961	-.0081	-.0111	03d (1.2500)	.0133
02s' (1.5729)	.0141	.3714	-.3687	H2p (0.9250)	.0958
02p' (1.0227)	.0067	-.0065	.2047		
02p'' (3.7596)	-.0053	.0074	.1777		
H1s (1.1986)	-.0027	.1507	.4723		
H2s (2.3003)	-.1816	-.3336	-.1403		
H1s' (2.4385)	-.0014	.0494	.0024		

Table A2

Summary of Detachment Energies for OH^-

Detachment Energy (eV)	Source
1.773	EOM ²
1.825 ± 0.002	Hotop, Patterson, Lineberger ^a
1.83	Branscomb ^b

a. Hotop, Patterson, Lineberger, J. Chem. Phys., 60, 1806 (1974).

b. L. M. Branscomb, Phys. Rev., 148, 11 (1966).

B. BeH^- : An Experimentally Understudied Anion

An initial basis set for the closed-shell ($1\sum^+$) BeH^- consisting of 20 Slater-type orbitals (STO's) was adapted from the optimized BeH basis set reported by Cade and Huo.⁵⁴ To accommodate the extra electron correlation, $2p_\pi$ functions and diffuse s and $2p_\sigma$ functions were added to the "sigma only" BeH basis set to replace functions contributing nominally to the description of the occupied BeH molecular orbitals.

The orbital exponents of the four BeH^- STO's in the original basis set having the largest expansion coefficients in the 3σ highest occupied molecular orbital (HOMO) were optimized at the initially calculated BeH^- equilibrium internuclear distance of 2.660 au. The initial and optimized BeH^- basis sets and expansion coefficients for occupied molecular orbitals are listed in Table B1. Basis functions which were also used in the Cade and Huo BeH basis set have been marked with an asterisk. From this table we observe that optimization of the BeH^- basis set caused dramatic increases in the importance of the diffuse $2s_{\text{Be}}$ and $1s_{\text{H}}$ basis functions describing the 3σ HOMO. SCF calculations for $E_{\text{BeH}^-}(\text{R})$ were executed on the University of Utah Univac 1108 computer using a modified version of the Harris DIATOM program. Execution time for each run was approximately 4.50 minutes. Vertical ionization energies of BeH^- , $\text{IP}_{\text{BeH}^-}(\text{R})$, were calculated by our third order equations-of-motion program. Execution time for each ionization energy calculation on the Univac 1108 was approximately 25 seconds. BeH energies were calculated by adding the vertical ionization energy of BeH^- to the BeH^- energy,

$$E_{\text{BeH}}(\text{R}) = E_{\text{BeH}^-}(\text{R}) + \text{IP}_{\text{BeH}^-}(\text{R}) \quad (23)$$

Table B1 Original and optimized 20 STO basis sets for BeH⁺. Original basis set; $R_e = 2.660$ au, $E = -15.12104$ au, $\epsilon_{1\sigma} = -4.51210$ au, $\epsilon_{2\sigma} = -0.28926$ au, $\epsilon_{3\sigma} = -0.02052$ au; IP = 0.02751 au. Optimized basis set; $R_e = 2.670$ au, $E = -15.12308$ au, $\epsilon_{1\sigma} = -4.50693$ au, $\epsilon_{2\sigma} = -0.27730$ au, $\epsilon_{3\sigma} = -0.01877$ au, IP = 0.02913 au.

BeH Basis	Orbital	ζ (original)	ζ (optimized)	$C_{1\sigma}$ (or.)	$C_{1\sigma}$ (op.)	$C_{2\sigma}$ (or.)	$C_{2\sigma}$ (op.)	$C_{3\sigma}$ (or.)	$C_{3\sigma}$ (op.)
*	1sBe	2.9443		0.84577	0.85361	-0.16987	-0.15081	-0.09822	-0.08297
*	1s'Be	5.7480		0.23092	0.22616	-0.00186	-0.01322	-0.01053	-0.01590
	2sBe	0.4000	0.4250	0.01243	-0.05928	0.01391	-0.09120	0.63441	1.08018
*	2s'Be	0.8925	1.1500	0.07154	0.10249	0.29861	0.39163	0.63860	0.56853
	2s''Be	1.7238		-0.11599	-0.16373	0.12175	-0.02363	0.06845	-0.05473
*	2p _σ Be	0.4000		0.01257	-0.01303	0.03299	-0.03817	-0.13953	-0.01732
	2p _σ 'Be	0.8080		0.03336	0.01491	0.05954	-0.01068	-0.11016	-0.28577
*	2p _σ ''Be	1.0460		-0.04211	-0.00897	0.12792	0.13522	-0.08124	0.05031
*	2p _σ '''Be	1.5000		0.01356	0.00193	0.09623	0.08734	-0.10446	-0.12637
	2p _π Be	0.8080		0.0	0.0	0.0	0.0	0.0	0.0
	2p _π 'Be	1.0460		0.0	0.0	0.0	0.0	0.0	0.0
	2p _π ''Be	1.5000		0.0	0.0	0.0	0.0	0.0	0.0
	1sH	0.4000	0.3000	-0.05489	0.03915	0.05648	0.15939	-0.47443	-0.73778
	1s'H	1.0000	1.0500	0.01772	-0.02409	0.71242	0.64323	-0.19299	-0.19021
*	2sH	2.5000		-0.00019	0.01496	0.01453	-0.01514	0.00898	0.00633
	2p _π H	1.4500		0.0	0.0	0.0	0.0	0.0	0.0

Approximate vibrational force constants (Table B2) and fundamental vibrational frequencies for the BeH and BeH⁻ systems were obtained by fitting a least squares quadratic polynomial to each potential energy curve. Agreement of these calculations with the experimental BeH values was quite good. For the original basis set, ν_e (calc.) - ν_e (exp.) was +44.6 cm⁻¹, a +2.17% deviation, and for the optimized basis set the deviation was -60.0 cm⁻¹ or -2.91%. For comparison, the value for ν_e^{BeH} reported by Cade and Huo deviated from the experimental value by +95.0 cm⁻¹ or +4.66%. It is reasonable to assume our calculated fundamental vibrational frequencies for BeH⁻ are at least this accurate.

In reporting Feldmann's value for IP_{BeH}⁻-(Thermo.) of 0.74 eV in Table B2, we have subtracted 0.01 eV (zero-point corrections) from the BeH⁻ photodetachment energy value of 0.75 eV. Calculated thermodynamic ionization potentials for BeH⁻ deviate from the experimental value by [-0.01 eV, -1.4%]^(or.), [+0.03 eV, +4.1%]^(op.). Vertical ionization energies and electron affinities differ no more than 7% from the experimental thermodynamic value. These results indicate that for reasonable approximations to the thermodynamic ionization energy of BeH⁻ our vertical EOM ionization energy calculations at R_e^{BeH} and $R_e^{\text{BeH}^-}$ are quite good.

Table B2. Calculated and experimental spectroscopic parameters for BeH and BeH⁻

Parameter	Units	BeH ⁻ (exp.)	BeH ⁻ (HF)	BeH ⁻ (or.)	BeH ⁻ (op.)	BeH ⁻ (or.)	BeH ⁻ (op.)	BeH ⁻ (exp.)
R _e	au	2.538 ^a	2.528 ^c	2.540	2.560	2.660	2.670	
k _e	dyne/cm x 10 ⁻¹	2.246 ^{a,h}	2.461 ^c	2.345	2.118	1.903	1.753	
ν _e	cm ⁻¹	2058.6 ^a	2154.6 ^{c,h}	2103.2 ^h	1998.6 ^h	1894.9 ^h	1818.5 ^h	
D _e	eV	(2.33) ^{a,b}	2.18 ^c			2.15 ^e 2.31 ^f	2.20 ^{d,e} 2.35 ^{d,f}	
EA _{BeH⁻} (R _e ^{BeH⁻})	eV			0.7031	0.7560			23
IP _{BeH⁻} (R _e ^{BeH⁻})	eV					0.7485	0.7926 ^d	
IP _{BeH⁻} (Thermo.)	eV					0.7253	0.7727 ^d	0.74 ^g

^a Herzberg, ref. (55).

^b Gaydon, ref. (56), reports 2.3 eV with an uncertainty of ±0.3 eV.

^c Cade and Huo, ref. (54).

^d Calculated from Cade and Huo HF D_e^{BeH⁻} of 2.18 eV.

^e Calculated from Herzberg's D_e^{BeH⁻} of 2.33 eV.

^f Feldmann, ref. (57), photodetachment energy value corrected for zero point vibrational energy difference by Eq. (19).

^g Calculated from k_e or ν_e assuming ν_e = $\frac{1}{2}\pi c \sqrt{k_e/\mu}$

C. CN^- and BO^- : A Well-Known Ligand and its Isoelectronic Partner

The starting point for the construction of the double zeta basis sets used in these calculations was Roetti and Clementi's excellent set⁵⁸ of double zeta functions for the component atoms. To better describe the charge distribution in the resultant negative molecular ions, the orbital exponents of the functions with large expansion coefficients in the highest occupied molecular orbital (HOMO) of CN^- and of BO^- were varied to maximize the ionization energies. The greatest changes in each case were produced by modifying the exponents of the 2s and $2p\sigma$ functions on the less electronegative atom in the ion.

Since little is known about the geometry of BO^- , its basis set was optimized at $R = 2.278$ bohr, which corresponds to the equilibrium separation of the neutral BO molecule. The total energy before optimization was -99.550 hartree and the corresponding $X^1\Sigma^+ \rightarrow X^2\Sigma^+$ ionization potential was 2.16 eV. The final basis gave a slightly lower SCF energy, -99.554 hartree, and a vertical ionization potential of 2.81 eV.

The CN^- basis set optimizations were performed at $R = 2.2$ bohr, the internuclear separation corresponding to the lowest energy found after a few preliminary SCF calculations on CN^- with the starting basis. The initial energy at 2.2 bohr was -92.2634 hartree, and the vertical ionization energy for the starting basis was 3.04 eV. After optimization of 2s and $2p\sigma$ functions on carbon and 2s functions on nitrogen, the total energy was -92.2645 hartree and the $X^1\Sigma^+ \rightarrow X^2\Sigma^+$ vertical ionization energy was 3.69 eV. The diffuse $2p\pi$ function on nitrogen was varied slightly in an attempt to obtain a reasonable $^1\Sigma \rightarrow ^2\pi$ ionization potential. However, the $^2\pi$ state of CN is not expected to be well described in our basis since the optimization of the pi functions was not extensive. The final optimized CN^- and BO^- basis sets

shown in Table C1 were used to compute ion-molecule energy differences at several internuclear separations; these differences were added to the total SCF energies at corresponding R values of the negative ions to generate SCF-level potential curves for BO and CN.

Examination of the ground state potential curves for BO, BO⁻, CN and CN⁻ allows us to determine the adiabatic electron affinities of BO and CN, which we can compare with existing experimental data. Our predicted electron affinity for BO, $2.79 \pm .2$ eV, is within the range of experimental estimates⁵⁹ which vary from 2.4 eV to $3.1 \pm .1$ eV. Experimental studies of CN have yielded more precise results. Chupka, *et al*⁶⁰, have reported an electron affinity of $3.82 \pm .02$ eV, which was obtained from photodissociation measurements on HCN. Our calculated electron affinity, $3.70 \pm .2$ eV, is in good agreement with this value.

The results of our EOM calculations and Koopmans' theorem estimates for vertical ionization potentials of CN⁻ and BO⁻ are shown in Table C2 for selected internuclear separations. The Koopmans' theorem values deviate considerably from EOM results for the $1\sum^+ \rightarrow 2\sum^+$ ionization of CN⁻, less so for the $1\sum^+ \rightarrow 2\sum^+$ BO⁻ ionization, and are actually very close to EOM results for the $1\sum^+ \rightarrow 2\pi$ ionization of CN⁻.

The large difference between Koopmans' theorem and the equations-of-motion result for the $1\sum^+ \rightarrow 2\sum^+$ ionization of CN⁻ indicates that orbital relaxation and electron correlation effects are important in the process of removing an electron from the 5 σ orbital of CN⁻. Analogously, relaxation and correlation effects appear to be less important in the ionization of BO⁻.

THE FINDINGS IN THIS REPORT ARE NOT TO BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, UNLESS SO DESIGNATED BY OTHER AUTHORIZED DOCUMENTS.

26

CN ⁻						BO ⁻					
σ orbitals			π orbitals			σ orbitals			π orbitals		
center	nl	ζ	center	nl	ζ	center	nl	ζ	center	nl	ζ
C	1s	5.1231	C	2p	1.2566	B	1s	4.2493	B	2p	.9500
C	1s	7.5223	C	2p	2.7304	B	1s	6.5666	B	2p	2.2173
C	2s	.9750	N	2p	1.3380	B	2s	.8250	O	2p	1.5200
C	2s	1.9400	N	2p	3.2493	B	2s	1.6500	O	2p	3.6944
C	2p	1.2566				B	2p	.8500			
C	2p	2.8700				B	2p	2.2173			
N	1s	5.9864				O	1s	6.8377			
N	1s	8.4960				O	1s	9.4663			
N	2s	2.3500				O	2s	2.8200			
N	2s	1.3750				O	2s	1.6754			
N	2p	1.4992				O	2p	1.6586			
N	2p	3.2493				O	2p	3.6944			

References and Footnotes

1. R. S. Berry, Chem. Rev. 69, 533 (1969).
2. W. D. Smith, T. T. Chen and J. Simons, "Theoretical Studies of Molecular Ions. Vertical Detachment Energy of OH^- ", Chem. Phys. Lett. 27, 499 (1974).
3. L. M. Branscomb, Phys. Rev. 148, 11 (1966).
4. H. Hotop, T. A. Patterson and W. C. Lineberger, J. Chem. Phys. 60, 1806 (1974).
5. C. L. Pekeris, Phys. Rev. 112, 1649 (1958).
6. A. W. Weiss, Phys. Rev. 166, 70 (1968).
7. E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964); E. Clementi, Phys. Rev. 135, A980 (1964).
8. O. Sinanoglu and I. Oksuz, Phys. Rev. Lett. 21, 507 (1968).
9. H. S. Taylor and F. E. Harris, J. Chem. Phys. 39, 1012 (1963).
10. A. C. Wahl and T. L. Gilbert, Bull. Am. Phys. Soc. 10, 1097 (1965); W. T. Zemke, G. Das, and A. C. Wahl, Chem. Phys. Lett. 14, 310 (1972).
11. P. E. Cade, J. Chem. Phys. 47, 2390 (1967); Proc. Roy. Soc. 91, 842 (1967).
12. J. Simons and W. D. Smith, J. Chem. Phys. 58, 4899 (1973); J. Simons, "The Self-Consistent Determination of the Negative-Ion and Neutral-Molecule Wavefunctions in a Theory of Electron Affinities", Chem. Phys. Lett. 25, 122 (1974).
13. The pioneering work on EOM theory for excitation energies was done by McKoy; T. Shibuya and V. McKoy, J. Chem. Phys. 53, 3308 (1970); *ibid.* 54, 1738 (1970); Phys. Rev. A2, 2208 (1970); T. H. Dunning and V. McKoy, J. Chem. Phys. 47, 1735 (1967); *ibid.* 48, 5263; T. Shibuya, J. Rose, and V. McKoy, J. Chem. Phys. 58, 500 (1973); J. Rose, T. Shibuya, and V. McKoy, J. Chem. Phys. 60, 2700 (1974).

14. K. D. Jordan, T. T. Chen, and J. Simons, Chem. Phys. 14, 145 (1976).
15. P. Jørgensen and J. Simons, J. Chem. Phys. 63, 5302 (1975).
16. L. S. Cederbaum, Theoretica Chem. Acta 31, 239 (1973); L. S. Cederbaum, G. Holneicher and S. Peyerimhoff, Chem. Phys. Lett. 11, 421 (1971); L. S. Cederbaum, G. Holneicher and W. von Niessin, Chem. Phys. Lett. 18, 503 (1973).
17. B. T. Pickup and O. Goscinski, Mol. Phys. 26, 1013 (1973).
18. G. Purvis and Y. Öhrn, J. Chem. Phys. 60, 4063 (1974); J. Chem. Phys. 62, 2045 (1975).
19. F. Tsui and K. F. Freed, Chem. Phys. Lett. 32, 345 (1975).
20. K. Griffing and J. Simons, "Theoretical Studies of Molecular Ions. The Ionization Potentials and Electron Affinity of BH", J. Chem. Phys. 62, 535 (1975).
21. J. Kenney and J. Simons, "Theoretical Studies of Molecular Ions: BeH⁻", J. Chem. Phys. 62, 592 (1975).
22. K. Griffing and J. Simons, "Theoretical Studies of Molecular Ions. Ionization Potentials of CN⁻ and BO⁻", J. Chem. Phys. 64, 3610 (1976).
23. E. Andersen and J. Simons "A Calculation of the Electron Affinity of the Lithium Molecule", J. Chem. Phys. 64, 4548 (1976).
24. K. Griffing, J. Kenney, J. Simons and K. D. Jordan, "Theoretical Predictions of Stable Negative Ions: HF⁻, LiH⁻, NaH⁻, J. Chem. Phys. 63, 4073 (1975).
25. K. D. Jordan, K. M. Griffing, J. Kenney, E. L. Andersen and J. Simons, "Theoretical Study of Stable Negative Ions of Polar Molecules: NaH⁻, LiH⁻, LiF⁻, BeO⁻", J. Chem. Phys. 64, 4730 (1976).
26. E. Andersen and J. Simons, "A Calculation of the Photodetachment Energy of NH₂⁻", J. Chem. Phys. 00, 0000 (1977).
27. J. L. Carlsten, J. R. Peterson, and W. C. Lineberger, Chem. Phys. Lett. 37, 5 (1976).

28. E. Clementi and A. D. McLean, J. Chem. Phys. 39, 323 (1963).
29. D. B. Boyd and W. N. Lipscomb, J. Chem. Phys. 46, 910 (1967).
30. M. Krauss, J. Res. Natl. Bur. Std. 63A, 635 (1964); M. Krauss, D. Neumann, A. C. Wahl, G. Dass and W. Zemke, Phys. Prev. A7, 69 (1973).
31. M. M. Heaton, A. Pipano and J. J. Kaufman, Inter. J. Quant. Chem. 6, 181 (1972).
32. R. E. Kari and I. G. Csizmadia, J. Chem. Phys. 56, 4337 (1972); M. A. Robb and I. G. Csizmadia, Inter. J. Quant. Chem. 5, 605 (1971).
33. G. V. Pfeiffer, unpublished results, Princeton University (1967).
34. H. F. Popkie and W. H. Henneker, J. Chem. Phys. 55, 617 (1971).
35. A. D. McLean and M. Yoshimine, J. Chem. Phys. 46, 3682 (1967); Inter. J. Quant. Chem. 15, 313 (1967).
36. T. L. Gilbert and A. C. Wahl, Bull. Am. Phys. Soc. 10, 1097 (1965).
37. W. H. Fink and L. C. Allen (unpublished results).
38. M. Geller, L. Sachs and J. J. Kaufman, unpublished results, RIAS and Jet Propulsion Laboratory.
39. P. W. Thulstrup, E. W. Thulstrup, A. Andersen, and Y. Öhrn, J. Chem. Phys. 60, 3975 (1974).
40. S. D. Peyerimhoff, R. J. Buenker and L. C. Allen, J. Chem. Phys. 45, 734 (1966).
41. M. Heaton and R. Cowdry, J. Chem. Phys. 62, 3002 (1975).
42. P. K. Pearson, H. F. Schaefer III, J. H. Richardson, L. M. Stephenson, and J. I. Brauman, J.A.C.S. 96, 6778 (1974).
43. J. Linderberg and Y. Öhrn, Chem. Phys. Lett. 1, 295 (1967).
44. J. Linderberg and Y. Öhrn, "Propagators in Quantum Chemistry", (Academic, London, 1972).
45. J. D. Doll and W. P. Reinhardt, J. Chem. Phys. 57, 1169 (1972).

46. B. Schneider, H. S. Taylor and R. Yaris, Phys. Rev. A1, 855 (1970);
B. S. Yarlagadda, Gy. Csanak, H. S. Taylor, B. Schneider and R. Yaris,
Phys. Rev. A7, 146 (1973).
47. O. Goscinski and B. Lukman, Chem. Phys. Lett. 7, 573 (1970).
48. D. J. Rowe, Rev. Mod. Phys. 40, 153 (1968); D. J. Rowe, Phys. Rev. 175,
1283 (1968).
49. G. Purvis and Y. Öhrn, Chem. Phys. Lett. 33, 396 (1975).
50. L. Tyner Redmon, G. Purvis and Y. Öhrn, J. Chem. Phys. 63, 504 (1975).
51. B. H. Brandow, Rev. Mod. Phys. 39, 771 (1967).
52. P. Jørgensen and G. Purvis, J. Chem. Phys., (to be published).
53. P. E. Cade, J. Chem. Phys. 47, 2390 (1967).
54. P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 614 (1967).
55. G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., (D. Van Nostrand
Co., Princeton, 1961), p. 508.
56. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules",
3rd Ed., (Chapman and Hall, London, 1968), p. 264.
57. D. Feldman (private communication).
58. C. Roetti and E. Clementi, J. Chem. Phys. 60, 4725 (1974).
59. D. E. Jensen, J. Chem. Phys. 52, 3305 (1970); R. D. Srivastava, O. M. Uy
and M. Farber, Trans. Farad. Soc. 67, 2941 (1971).
60. J. Berkowitz, W. A. Chupka and T. A. Walter, J. Chem. Phys. 50, 1497 (1969).
61. E. Clementi, J. Chem. Phys. 38, 996 (1963).
62. G. Das, J. Chem. Phys. 46, 1568 (1967).
63. G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed. (Van Nostrand,
Princeton, 1961), p. 546.
64. V. F. Khrustov, N. F. Stepanov, S. S. Yarovoy, A. Va. Abramnikov, N. P.
Pashyunatie, Z. Ya. Tsirul, Vestn. Mosk. Univ., Kim. 12, 221 (1971).

65. R. Velasco, Ch. Ottinger, and R. N. Zare, J. Chem. Phys. 51, 5522 (1969).
66. T. A. Patterson, H. Hotop, A. Kasdan, D. W. Norcross and W. D. Lineberger, Phys. Rev. Lett. 32, 189 (1974).
67. P. H. Blustin and J. W. Linnett, J. Chem. Soc., Faraday Trans. 2, 70, 826 (1974).
68. G. A. Henderson, W. T. Zemke, and A. C. Wahl, J. Chem. Phys. 58, 2654 (1973).
69. C. Bottcher and A. Dalgarno, Chem. Phys. Lett. 36, 137 (1975).
70. K. M. Griffing, J. Kenney, J. Simons and K. D. Jordan, J. Chem. Phys. 63, 4073 (1975).
71. R. F. Wallis, R. Herman, and H. W. Milnes, J. Mol. Spect. 4, 51 (1960).
72. O. H. Crawford, Proc. Phys. Soc. 91, 279 (1967); O. H. Crawford, Mol. Phys. 20, 585 (1971).
73. C. A. Coulson and M. Walmsley, Proc. Phys. Soc. 91, 231 (1967).
74. O. H. Crawford and B. J. D. Koch, J. Chem. Phys. 60, 4512 (1974).
75. W. R. Garrett, Phys. Rev. A3, 961 (1971).
76. J. E. Turner, V. E. Anderson, and K. Fox, Phys. Rev. 174, 81 (1968).
77. K. D. Jordan and B. Luken, "Theoretical Study of the Binding of an Electron to a Molecular Dipole: LiCl^- ", J. Chem. Phys. 64, 2760 (1976).
78. M. Yoshimine, J. Chem. Phys. 40, 2790 (1964); J. Phys. Soc. Japan 25, 1100 (1968).
79. E. A. Andersen and J. Simons (to be published).
80. These SCF-MO calculations were performed using the Gaussian 70 package of W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, available as QCPE program 236, Indiana University. In this program, orbitals in the same shell share the same exponent.
81. K. D. Jordan, J. L. Kinsey, and R. Silbey, J. Chem. Phys. 61, 911 (1974); K. D. Jordan, J. Mol. Spectr. 56, 329 (1975).

82. K. K. Docken and J. Hinze, J. Chem. Phys. 57, 4928 (1972).
83. B. Steiner, J. Chem. Phys. 49, 5097 (1968).
84. P. W. Thulstrup and E. W. Thulstrup, Chem. Phys. Lett. 26, 144 (1974).
85. P. A. G. O'Hare, J. Chem. Phys. 54, 4124 (1971); P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 53, 2834 (1970); *ibid*, 54 4563 (1971)
86. The self-energy $\Sigma(E)$ is given by $\underline{A}^{(3)} + \underline{B} \underline{D}^{-1} \underline{C}$, where $\underline{A}^{(3)}$ is the third-order part of \underline{A} .
87. K. C. Smyth and J. I. Brauman, J. Chem. Phys. 56, 4620 (1972); R. J. Celotta, R. A. Bennett, and J. L. Hall, J. Chem. Phys. 60, 1740 (1974).
88. J. H. Richardson, L. M. Stephenson, and J. I. Brauman, Chem. Phys. Lett. 25, 318 (1974).
89. E. Herbst, T. A. Patterson, and W. C. Lineberger, J. Chem. Phys. 61, 1300 (1974).
90. K. D. Jordan (private communication).
91. P. D. Burrow and K. D. Jordan, Chem. Phys. Lett. 36, 594 (1975).
92. K. D. Jordan, Chem. Phys. Lett. 00, 0000 (1976).
93. K. D. Jordan and J. Simons, J. Chem. Phys. 65, 1601 (1976).
94. This result is in reasonable agreement with the preliminary SCF - CI results of D. A. Dixon, J. L. Gole, and K. D. Jordan (unpublished).